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DESIGN AND CHEMICAL SYNTHESIS OF IODINE-CONTAINING MOLECULES
FOR APPLICATION TO SOLAR-PUMPED I* LASERS

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We are exploring the design and chemical synthesis of new media for solar-pumped I* lasers. In an effort to prepare an iodo fluorocarbon compound absorbing strongly at 300 nm or above, we have investigated the synthesis of perfluoro allylic iodides. These compounds furnish especially stable allylic radicals upon photodissociation. We anticipated that the desired red shift in the absorption maximum could correlate with increasing radical stability. This expectation was based upon our analysis, previously reported to NASA, of the structures and absorption maxima of compounds studied earlier.

We have prepared a prototypical target molecule, perfluoro-3-iodocyclopent-1-ene (**1**), a previously unknown substance. We obtained **1** by reaction of perfluorocyclopentene with sulfur trioxide under the influence of antimony pentafluoride catalyst, followed by treatment of the resulting allylic fluorosulfonate with sodium iodide in sulfolane solvent.



As noted in our previous report, preliminary data indicate that the absorption maximum for **1**, at 272 nm, is not shifted significantly to longer wavelength. We cannot say whether this result reflects an unexpected influence of the cyclic structure of **1** upon the position of the absorption maximum. However, the available evidence suggests that perfluoroallyl iodides will not yield the requisite long-wavelength absorption.

For the detailed study of the photodissociation of **1**, to be carried out by my colleague Stephen R. Leone, the compound must be synthesized in multi-gram quantities. We have encountered some serious obstacles in the course of the latter undertaking. First, we found that the perfluoro-

cyclopentene starting material purchased from Alfa Products does not react with sulfur trioxide under the conditions we have employed, whereas satisfactory results are still obtainable with perfluorocyclopentene purchased from SCM Specialty Chemicals (formerly PCR). Although we can prepare the requisite synthetic intermediate using compound purchased from SCM, the procedure we will publish obviously should address the remarkable difference in the reactivities of these samples. As yet, however, we have been unable to ascertain the factor(s) responsible. The other notable difficulty in preparing the required amounts of 1 has been the inefficiency of the second synthetic step. We are currently investigating a possible side-reaction involving the fluorosulfonate intermediate and the sulfolane solvent employed for iodide displacement. This problem is not mentioned in connection with similar transformations reported in the Russian literature. We anticipate that an inert alternative solvent can be found, and experiments directed toward this objective are in progress.

As we have indicated previously, we do hope to explore briefly the potential of other classes of lasants despite the limited time and resources available for further studies. Current knowledge suggests that three other classes of lasants are most promising.

(i) We will prepare a prototypical lasant containing iodine atoms on adjacent carbons, $\text{ICF}_2\text{CF}_2\text{I}$. This substance, which has been reported earlier, is an attractive target because the Leone group previously observed large (ca. 20-fold) enhancements of absorption strengths in molecules containing halogens on adjacent carbon atoms. A gain of this magnitude in absorption intensity could compensate significantly for an absorption maximum at shorter wavelength than desired. The influence of a second iodine atom on the posi-

tion of the absorption maximum will also become apparent.

(ii) Our early efforts to prepare transition metal iodides bearing perfluoroalkyl substituents were thwarted by the finding that many such species (e.g., $(\text{CF}_3)_3\text{TiI}$) decompose readily via expulsion of difluorocarbene ($\text{F}_2\text{C:}$). This difficulty might be circumvented by preparing cyclopentadienyl-substituted species (i.e., compounds of type 2) which cannot fragment in this



fashion. One or more additional ligands on the metal will generally be present as well. A large number of compounds (ca. 1,000-2,000) containing this structural unit have been reported previously, and many of these possess absorption maxima in the 300-350 nm range. We are currently evaluating these structures.

(iii) As reported earlier, preliminary studies in the Leone group showed that BI_3 absorbs strongly at wavelengths greater than 300 nm and affords I^* upon photodissociation. Although this simple molecule was not expected to be a satisfactory lasing medium, this result does suggest that closely related species, $(\text{CF}_3)_2\text{BI}$ or BF_2I , may be effective. Synthesis of BF_2I appears more straightforward. We also note that $(\text{CF}_3)_2\text{BI}$ may decompose via loss of $\text{F}_2\text{C:}$, as we observed previously in the titanium series.